Time-resolved in-situ mass spectrometry for monitoring and identifying reaction products in ALD processes

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Several measurement techniques are available for *in-situ* monitoring of ALD processes. Microbalance, infrared spectroscopy and (spectroscopic) ellipsometry are well-established [1]. Compared to these techniques, the use of mass spectrometry is less common in the ALD field. Given the need for good time resolution, only a few masses can be studied simultaneously, often limiting the practical use of mass spectrometry to the detection of simple and small reaction products such as CH_4, CO and CO_2. For more complicated reaction chemistries, a time-resolved measurement of the full m/z-range is necessary, since this allows for fingerprinting reaction products by their entire mass-to-charge-spectrum instead of a single mass-to-charge ratio. A novel data acquisition method is described which allows for obtaining time-resolved, full mass-to-charge-range mass spectra to investigate ALD reaction chemistries. This method is demonstrated for the well-known TMA-H_2O ALD process for Al_2O_3 as a proof of concept, and its usefulness is further illustrated by its application to the LiHMDS-TMP process for the deposition of solid electrolyte Li_3PO_4 films reported by Hämäläinen *et al*. [2], as shown in figure 1.

The atomic layer deposition field proves an inherently difficult use case for mass spectrometry. In other fields where mass spectrometry is commonly employed (e.g. peptide synthesis), the source of molecules is quasi unlimited and there is only one species of interest to identify. In ALD process characterisation however, life is not that easy.
First of all, in an ALD process there is a background of precursor molecules/reactant gas with a known structure, which are of relatively little interest. The gaseous reaction products, which are of interest, are usually only present in small concentrations as they originate from the surface reactions in the reactor and are typically only present in the reaction chamber for a very limited time as they are continuously removed during the process. Measurements with good time resolution hence become paramount for a successful understanding of the reaction chemistry [3].
Secondly, it is impossible to distinguish the gaseous reaction products that originate from surface reactions on the reactor walls from those originating from the sample surface. This can be alleviated by increasing the signal-to-noise ratio (using a substrate with higher surface area) and considering proper background or baseline spectra.
Finally, since mass spectrometry relies on the ionizing and cracking of incoming molecules, the masses of detected fragments originating from the reaction products of interest are usually very similar to those of the originating precursor molecule. Spectral overlap compromises the assignment of a single m/z ratio to a molecule. This motivates the need for 'fingerprinting' complex by-products by their full spectrum.

Despite these hurdles, ALD processes have the advantage that they are of cyclic nature, so after the first cycles where initial growth effects could be of importance, the chemistry of each cycle should be identical and can be repeated as often as necessary to obtain data with good signal-to-noise ratio. In this work, we exploit this by combining data from several ALD cycles to construct a time-resolved m/z spectrum of the chemicals in one ALD cycle with a standard quadrupole mass spectrometer (Hiden HPR-30). This way, the aforementioned barriers can be surmounted, enabling complete mass spectrum analyses of ALD reaction chemistries.

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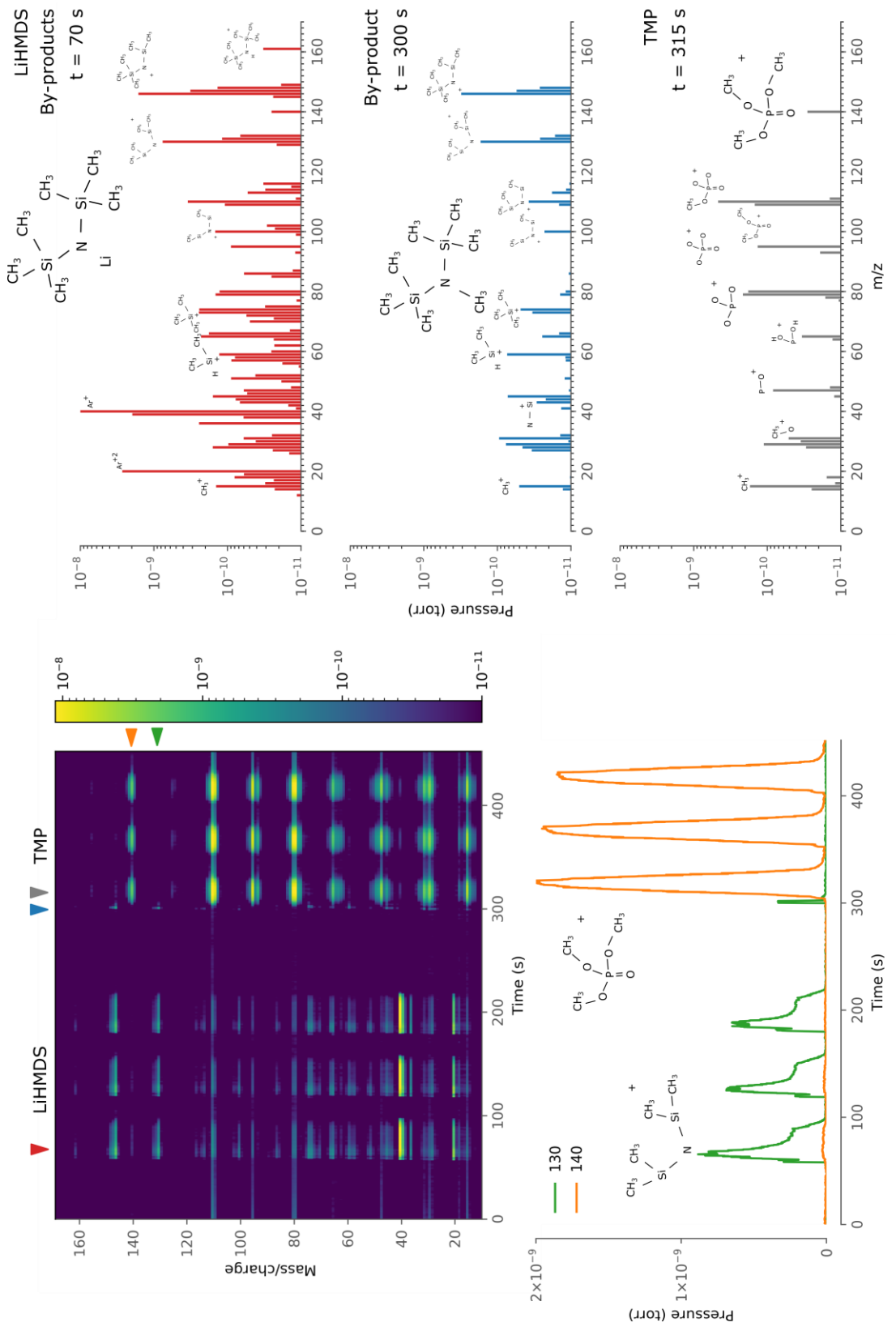

Figure 1. Illustration of the results obtained by the analysis method. Three pulses of lithium hexamethyl disilyl azide (LiHMDS) were followed by 3 pulses of trimethyl phosphate (TMP). This process results in a crystalline Li_3PO_4 film [2]. The heat map shows the full dataset, the other graphs are slices of a specific mass over charge ratio, similar to results obtained by a 'classical' measurement. The mass over charge spectra are taken at specific times indicated on the graphs. In this way the first pulse shows a sign of the reaction products, where the next pulses indicate the fingerprint of the precursor molecule. At t= 70 s, the LiHMDS peak is visible, together with groups from the TMP molecule that at that time are removed from the surface (red spectrum). A clear signature is visible at t=300, indicating that CH_3 from the TMP is taken by the $N(Si(CH_3)_3)_2$ ligand (blue spectrum). Finally the signature of the TMP precursor molecule (no reaction products) is observed at t = 315 s. Careful analysis of this kind of dataset can unravel the complex reaction mechanism.